Assessment of heavy metal and As behaviour in contaminated soils by pH_{stat} leaching

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Introduction

- CCP's determine fate of pollutants
- pH = key parameter for heavy metal mobility in soils and sediments
- Influence of pH on heavy metal mobility $\rightarrow$

pH_{stat} leaching tests

pH_{stat} tests

- Batch test for soils, sediments, waste material, ...
- Release of elements
  - as a function of pH
  - as a function of time
- Operationally defined

Equipment

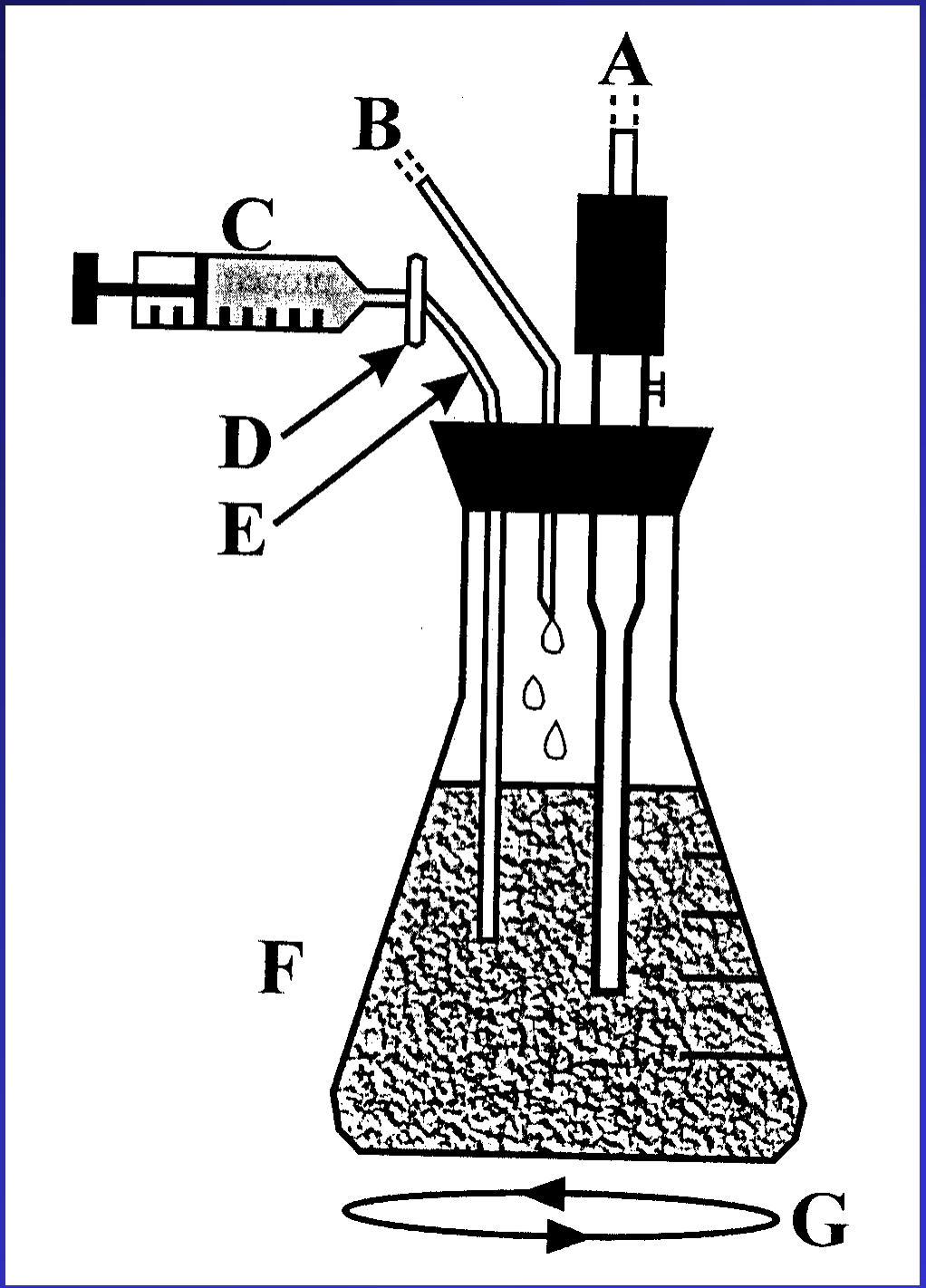
A. pH electrode

B. dispenser

C-D-E: Syringe with filter and flexible tube

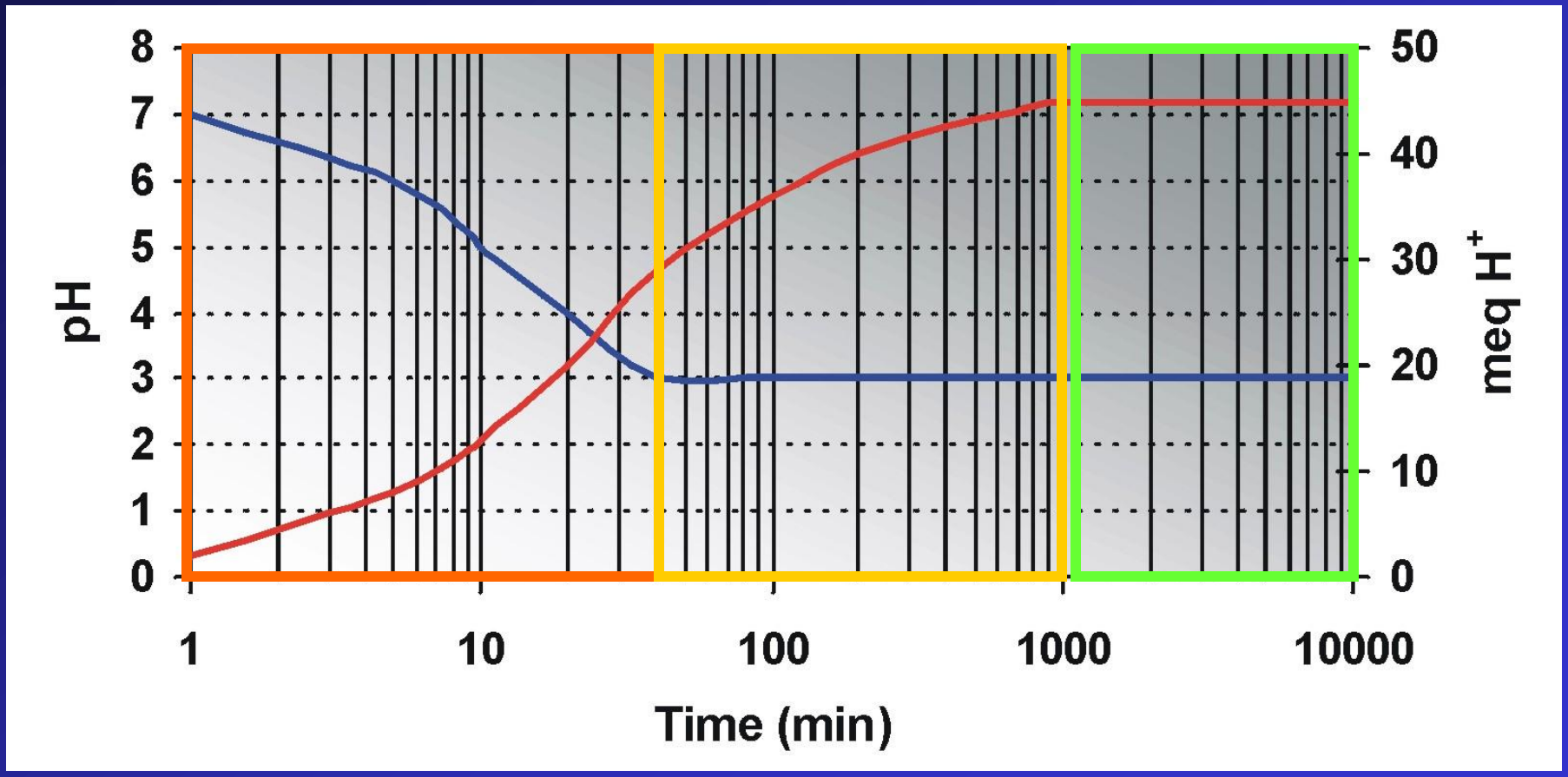
F: soil suspension

G: horizontal shaking table



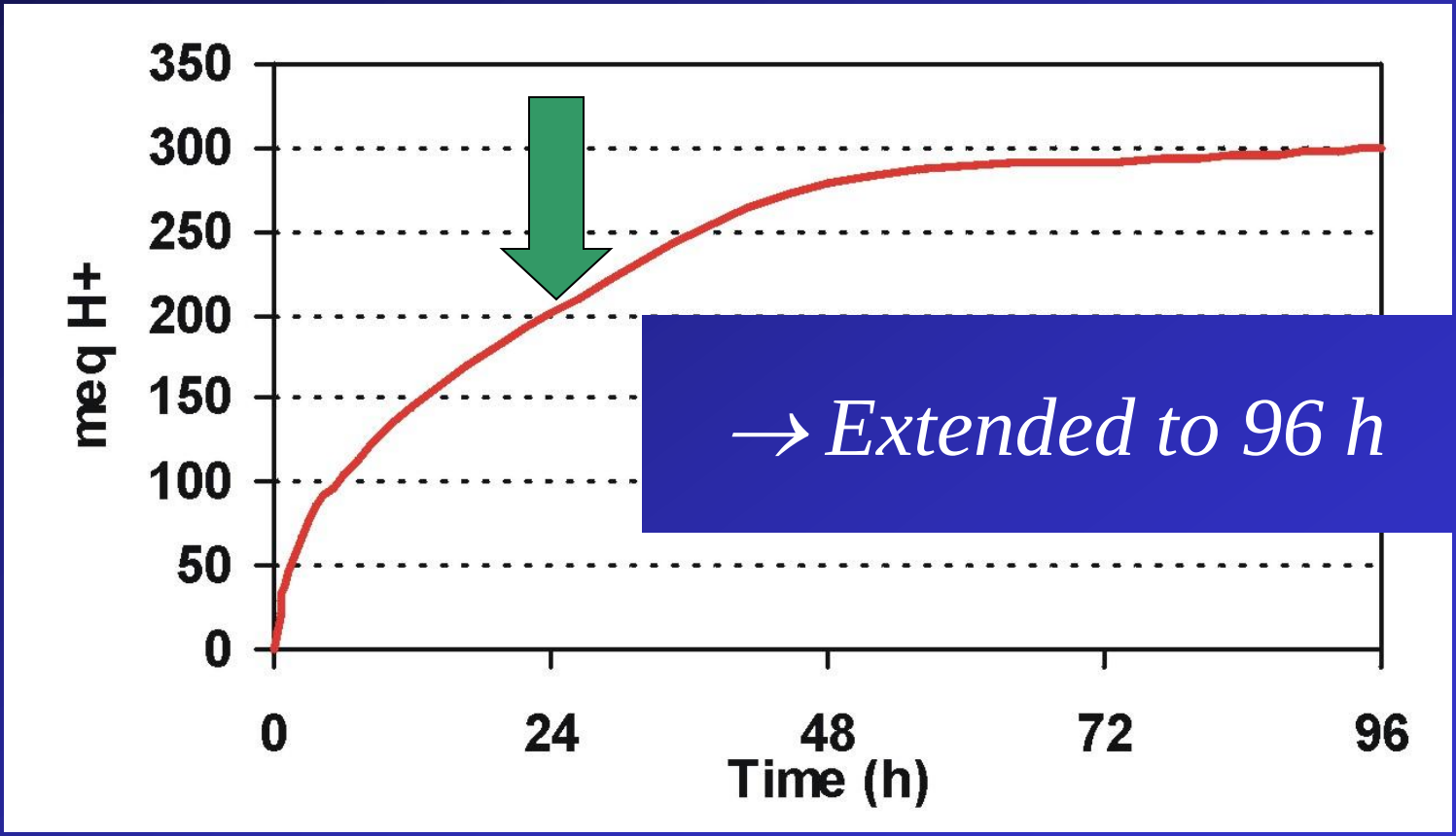
pH_{stat} titration : 3 steps

Step 1 ***Step 2*** ***Step 3***

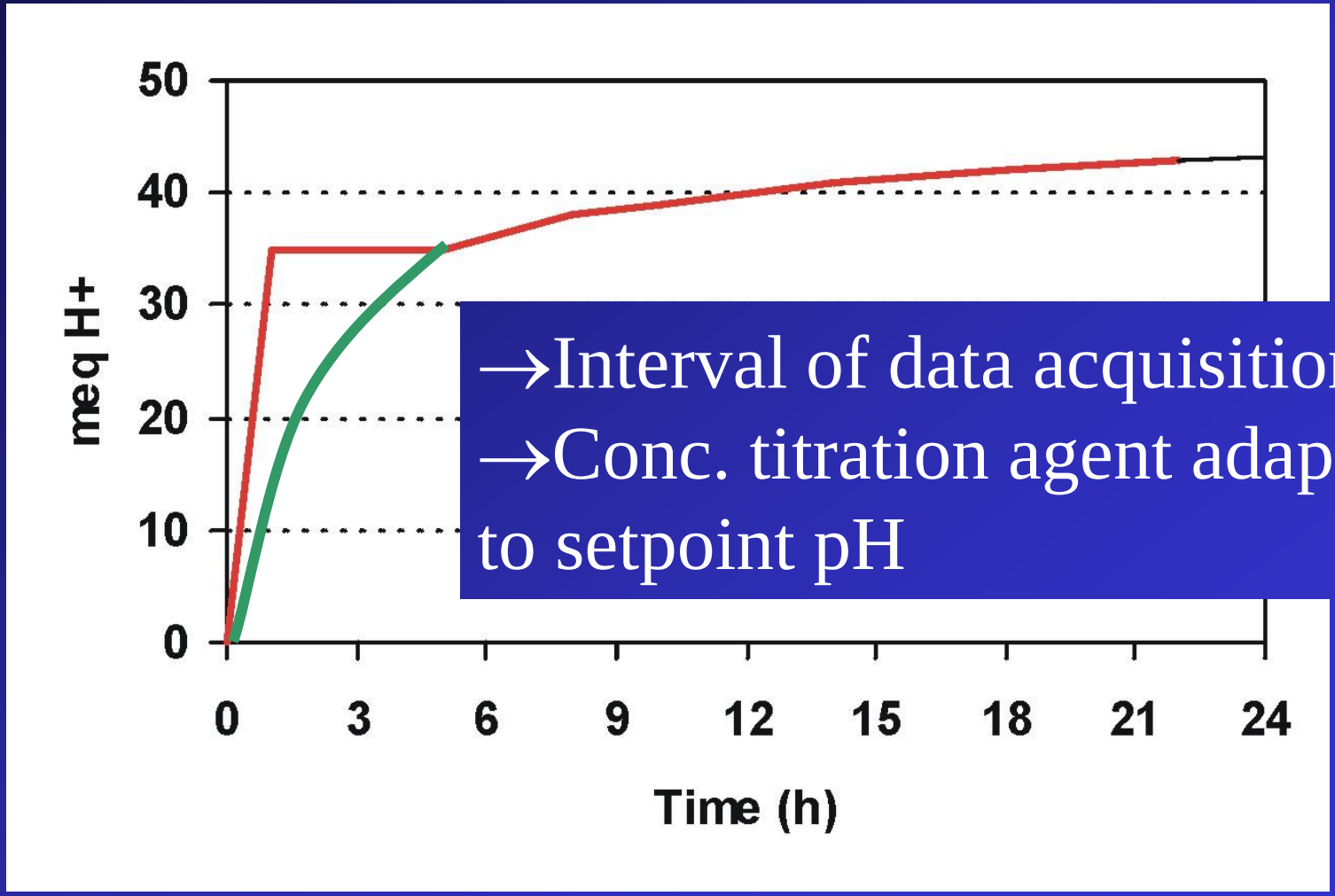


Optimization

1. Duration of pH_{stat} test



2. Titration too fast
3. Setpoint pH exceeded

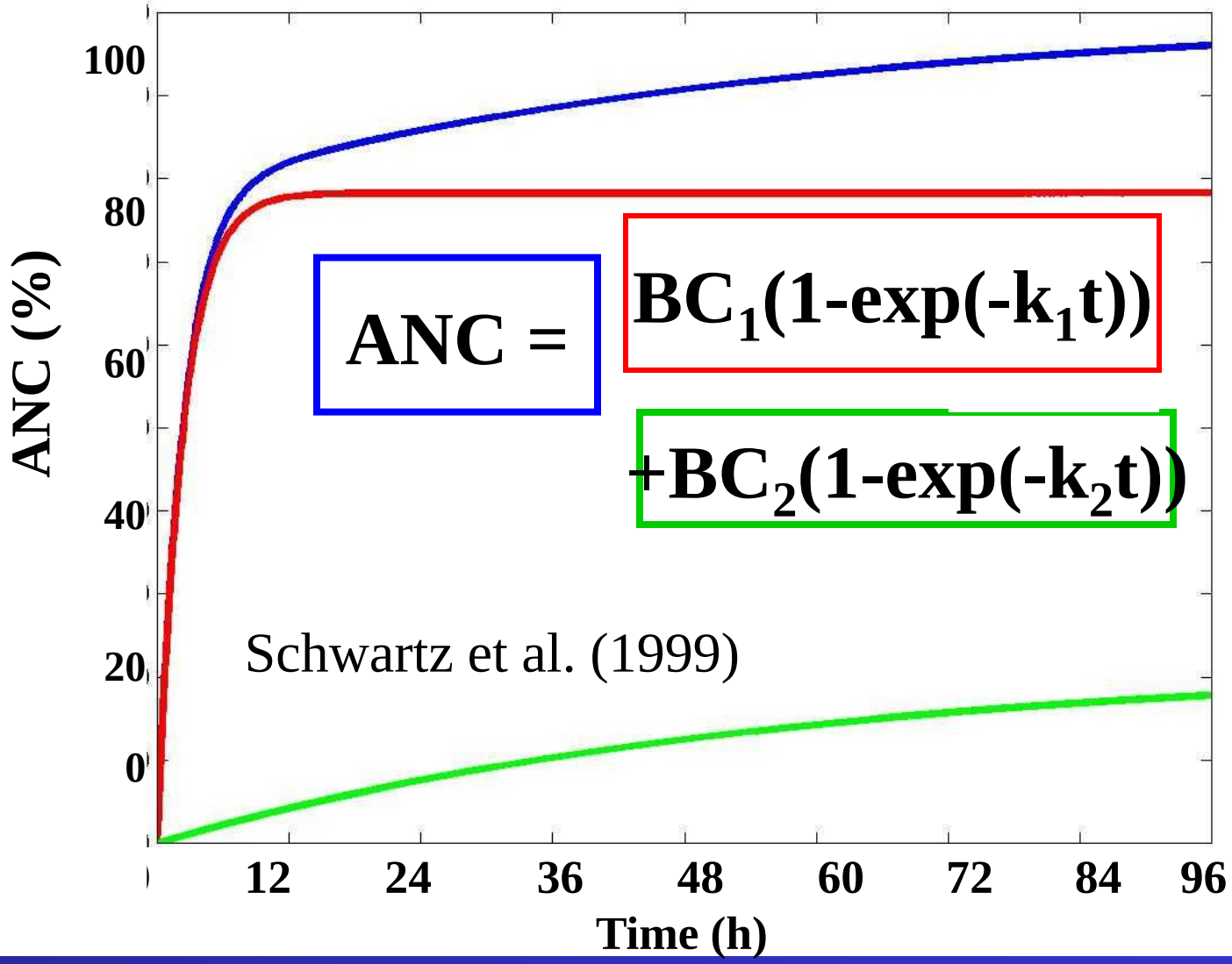


→Interval of data acquisition ↑
→Conc. titration agent adapted to setpoint pH

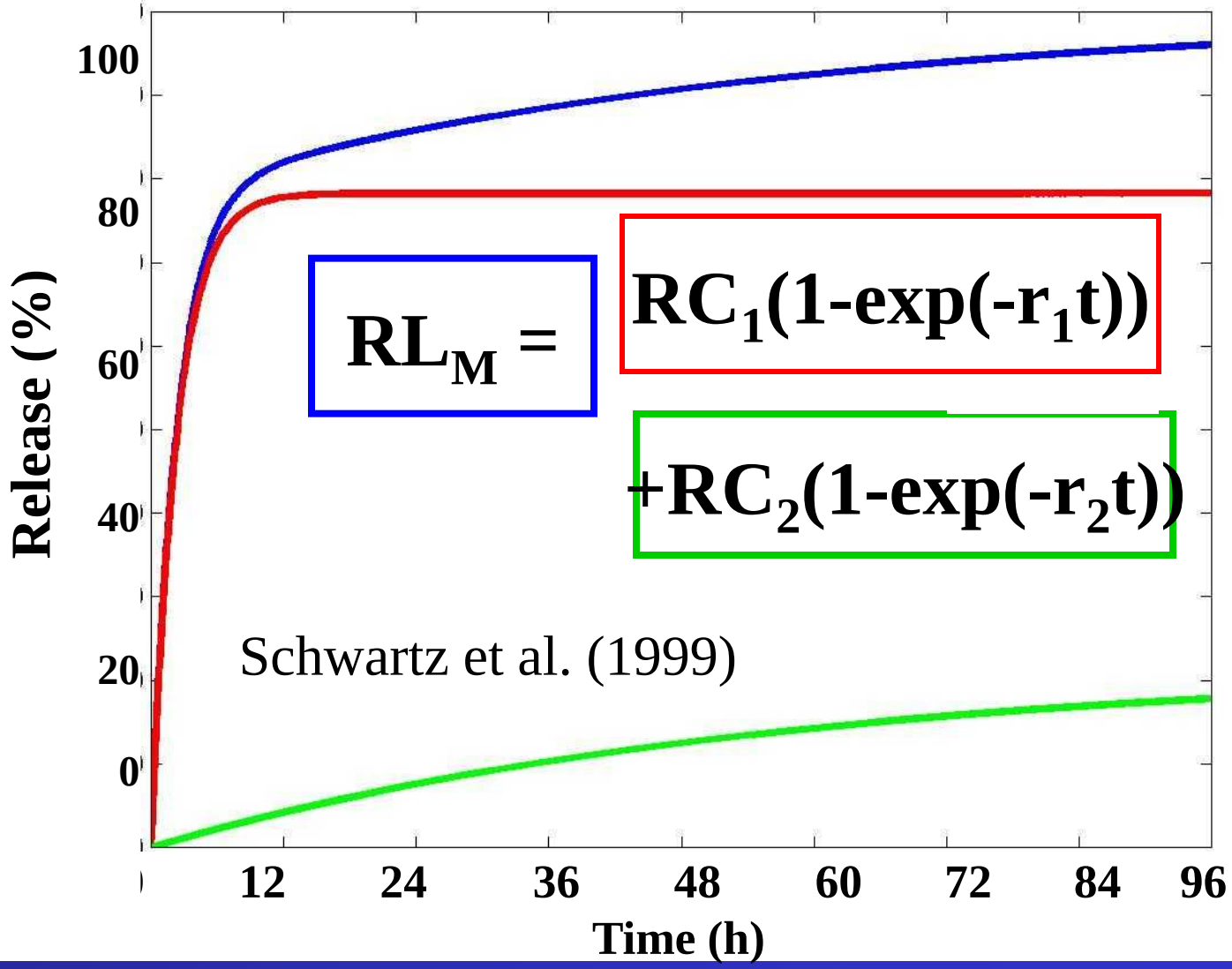
Applications: examples

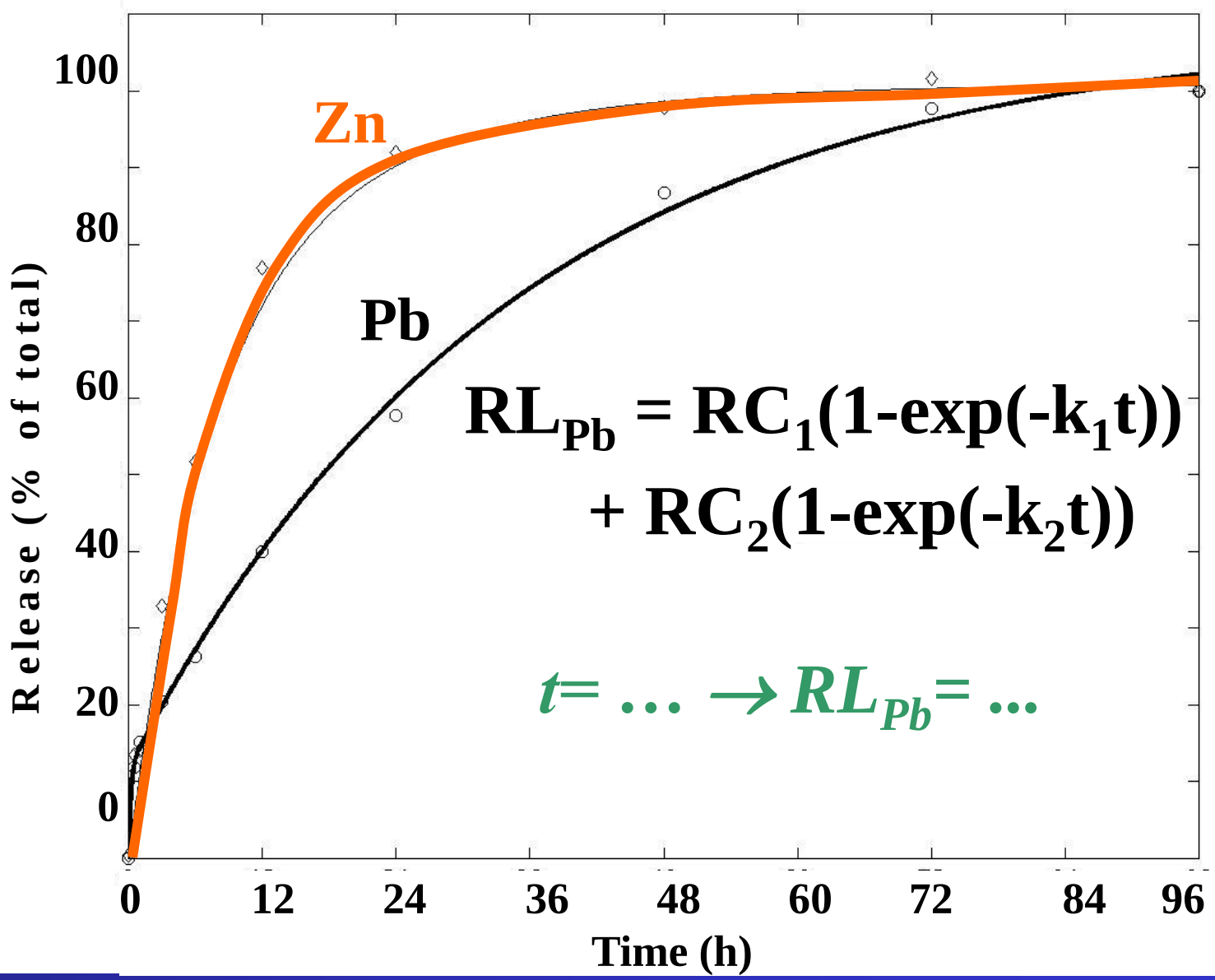
- Waste material
  - slag material from arsenic refinery
  - waste material from the roasting of pyrite
- Soils and sediments
  - soils from an industrial site
  - dredged sediments with ≠ time since disposal
  - overbank sediments polluted by industrial activities and mining

Modelling of ANC



Modelling of release kinetics

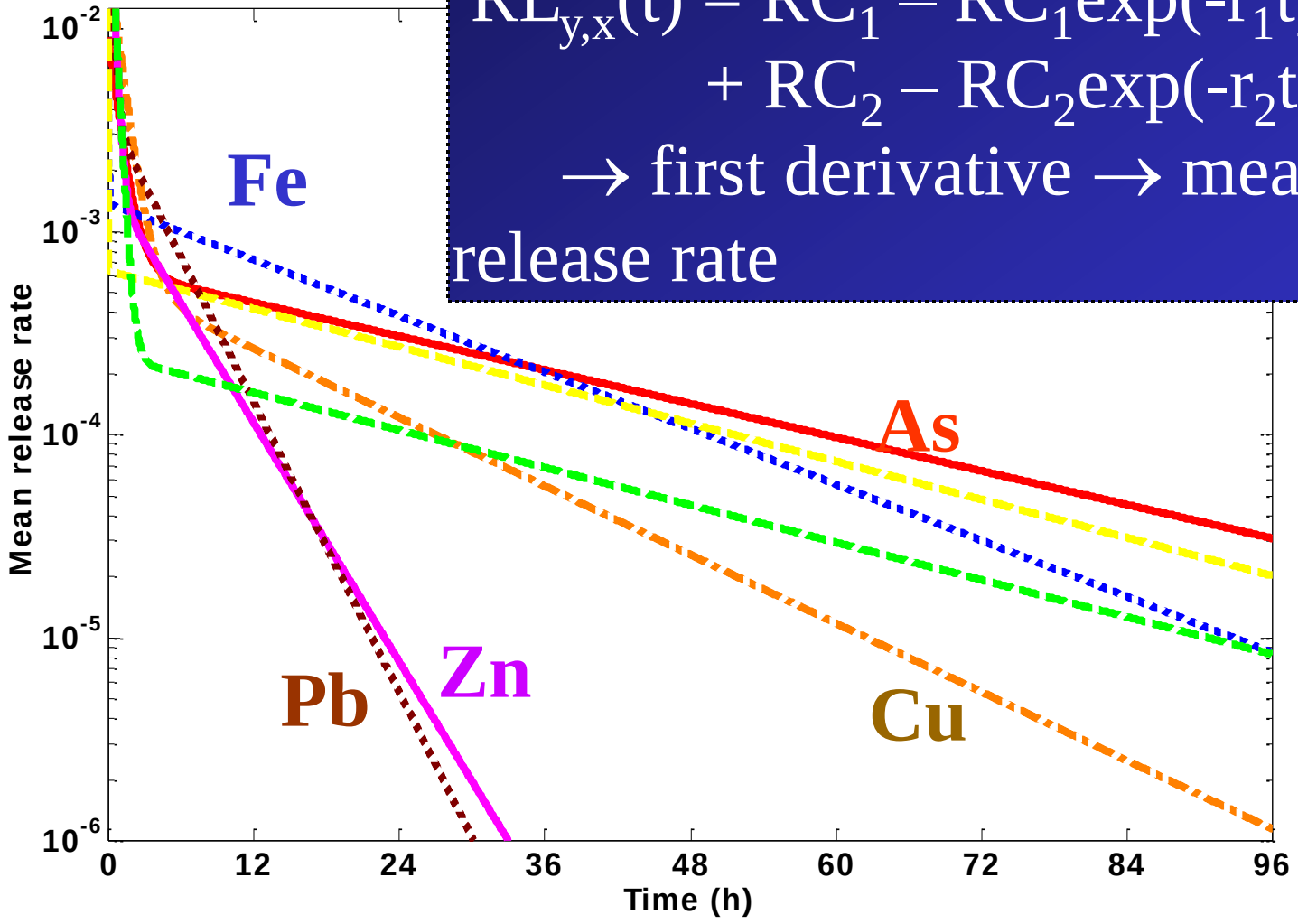



Zn
Pb
$RL_{Pb} = RC_1(1-\exp(-k_1 t)) + RC_2(1-\exp(-k_2 t))$
$t = \ldots \rightarrow RL_{Pb} = \ldots$
Release (% of total)
Time (h)
0
20
40
60
80
100
0
12
24
36
48
60
72
84
96

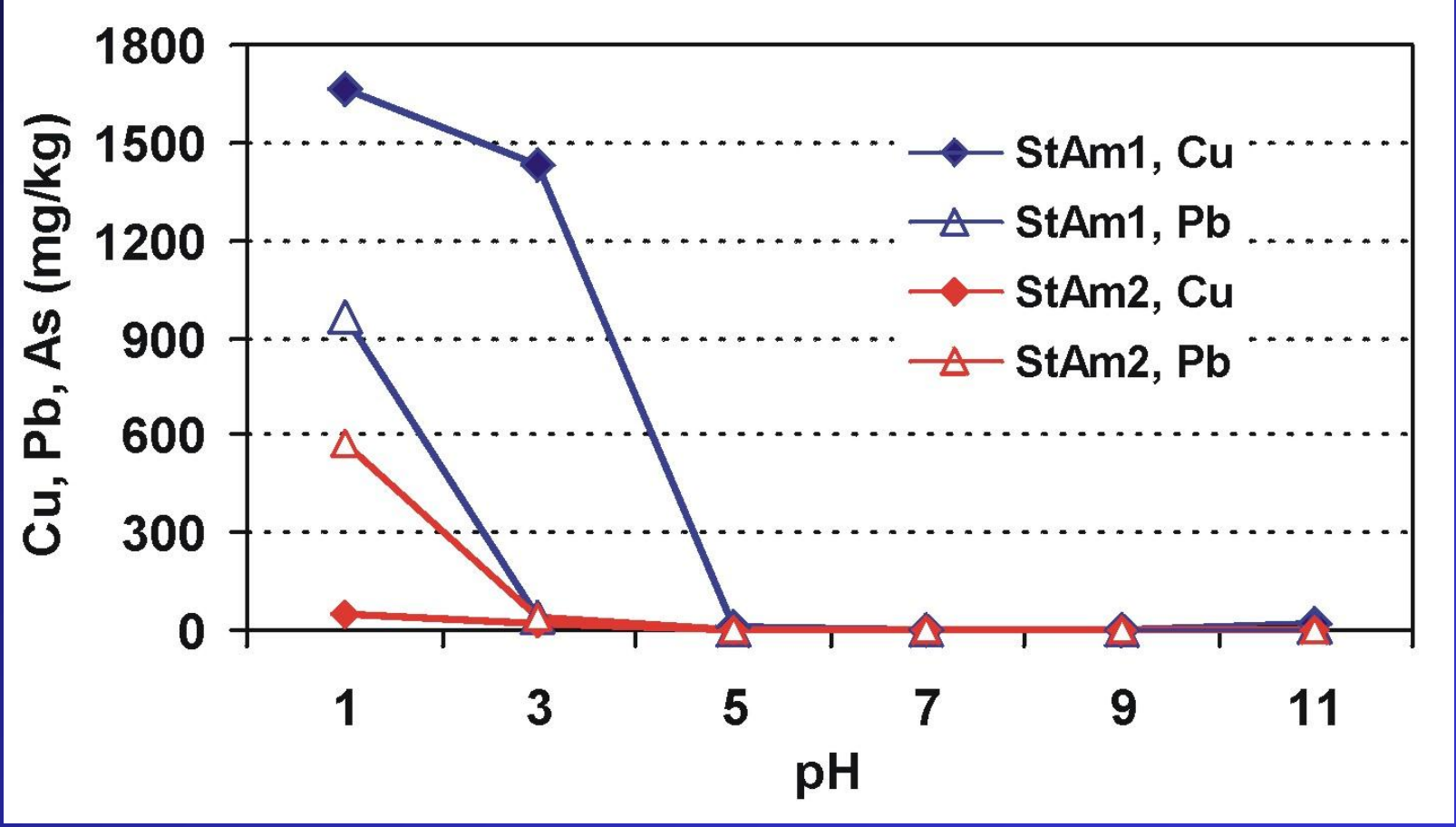
Release rate

$RL_{y,x}(t) = RC_1 - RC_1\exp(-r_1 t) + RC_2 - RC_2\exp(-r_2 t)$

$\rightarrow$ first derivative $\rightarrow$ mean release rate

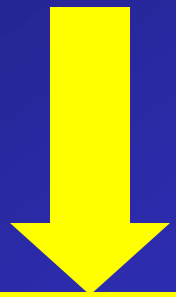


Leaching= f(pH)



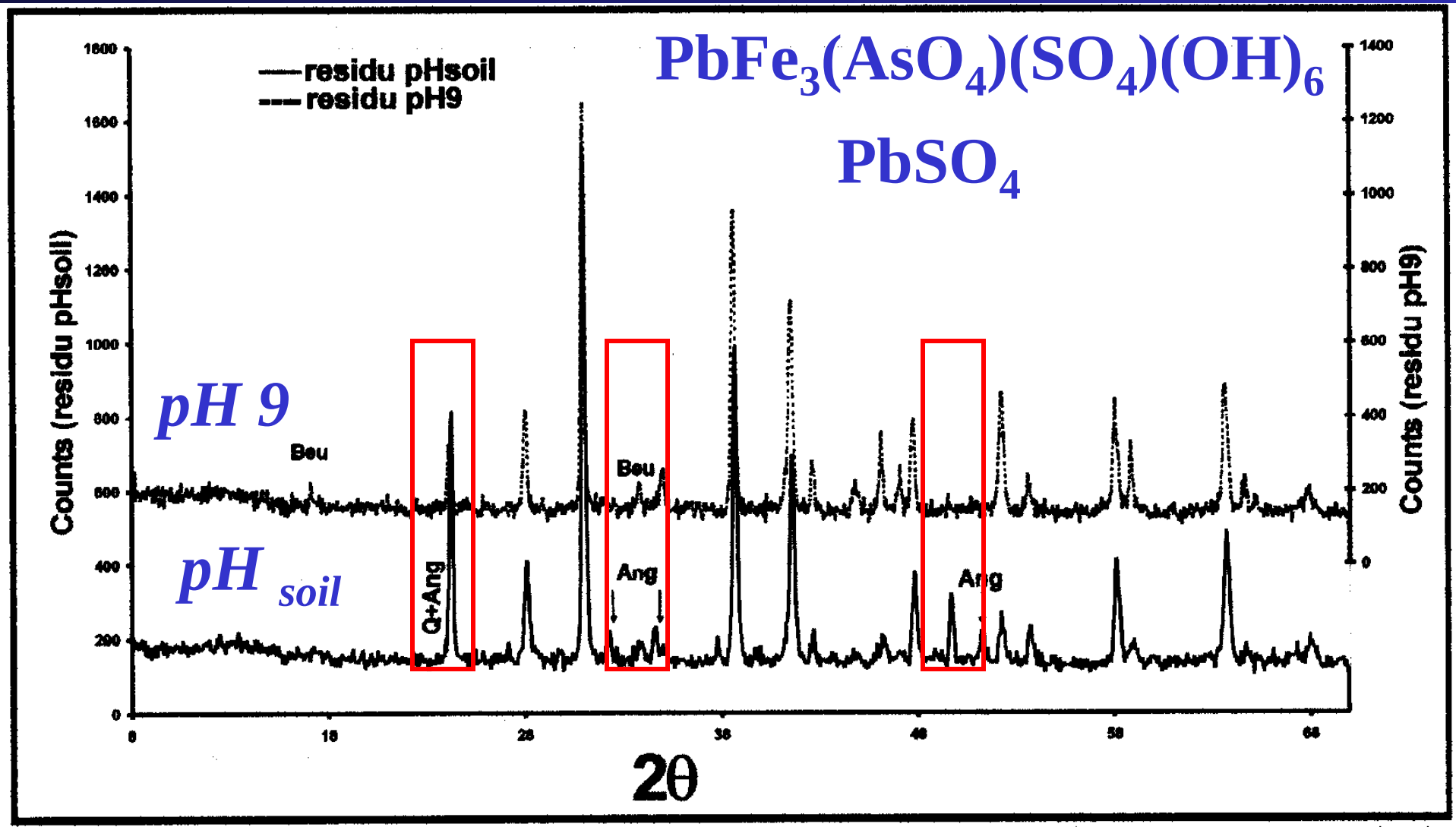
Mechanisms of heavy metal release

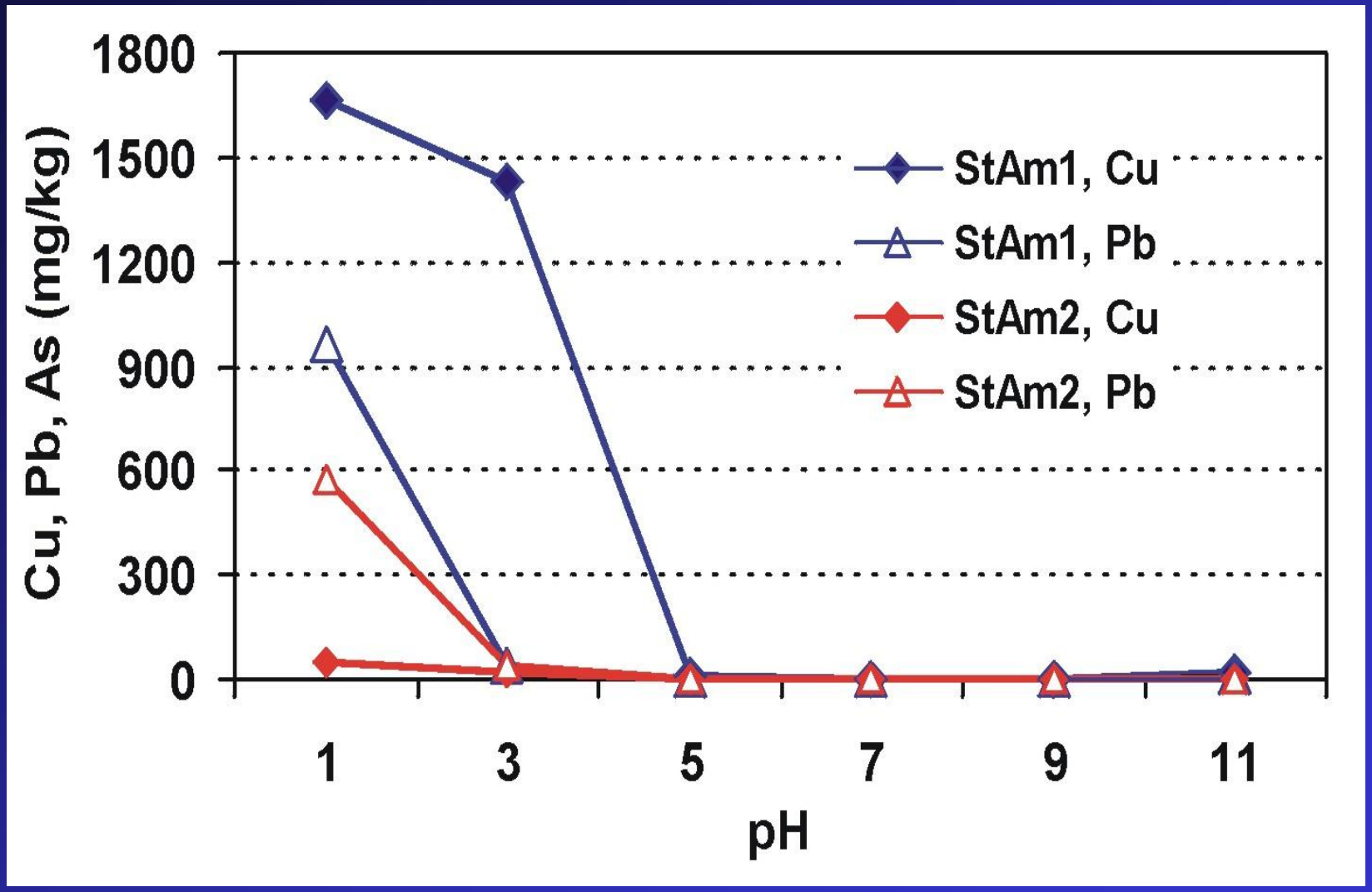
- Release of major elements (Fe, Ca)
- Release of anions (SO_4^{2-}, PO_4^{3-}) , DOC
- Mineralogy (before and after leaching)



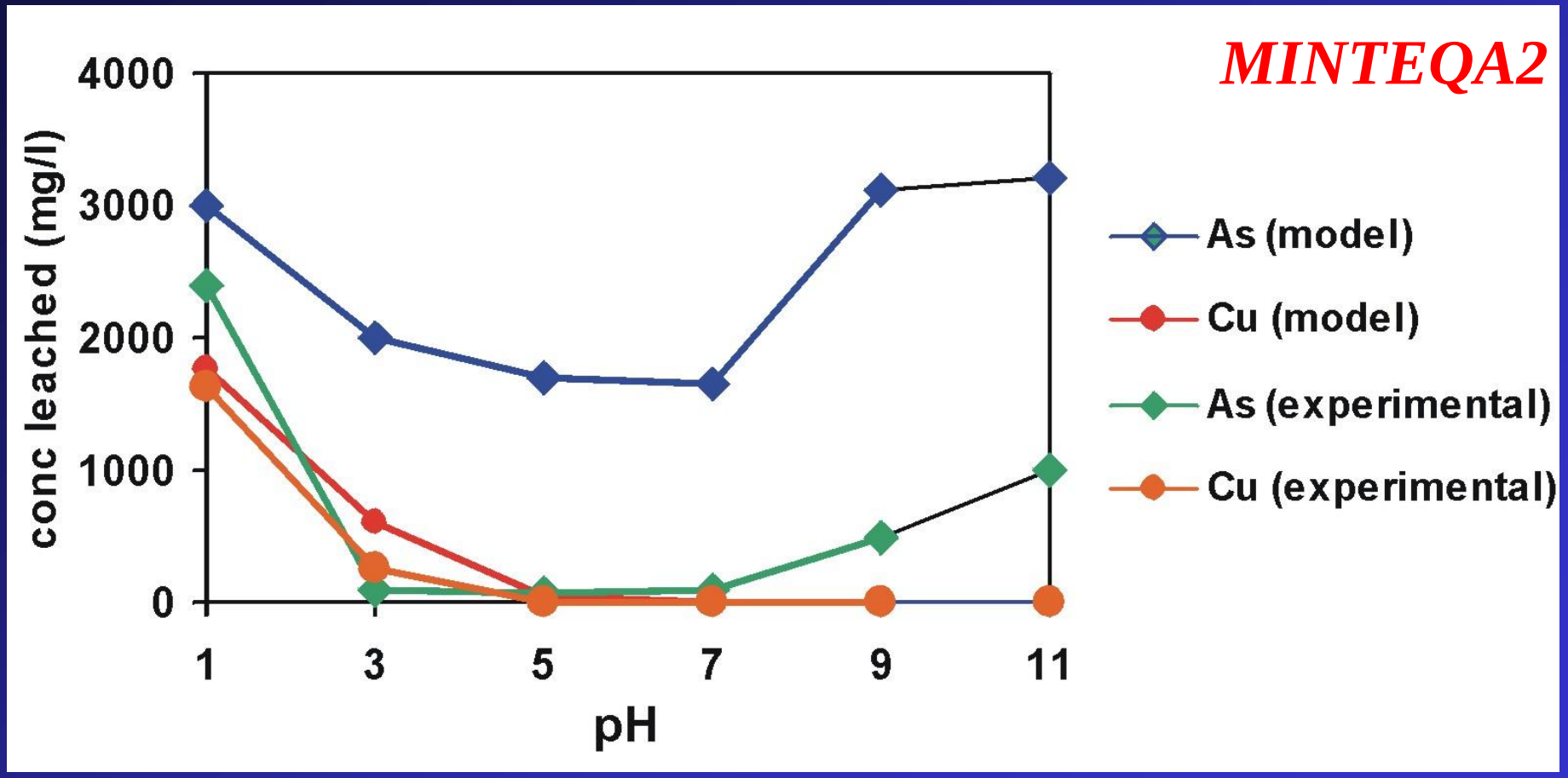
Geochemical modelling (MINTEQA2)

Sample mineralogy



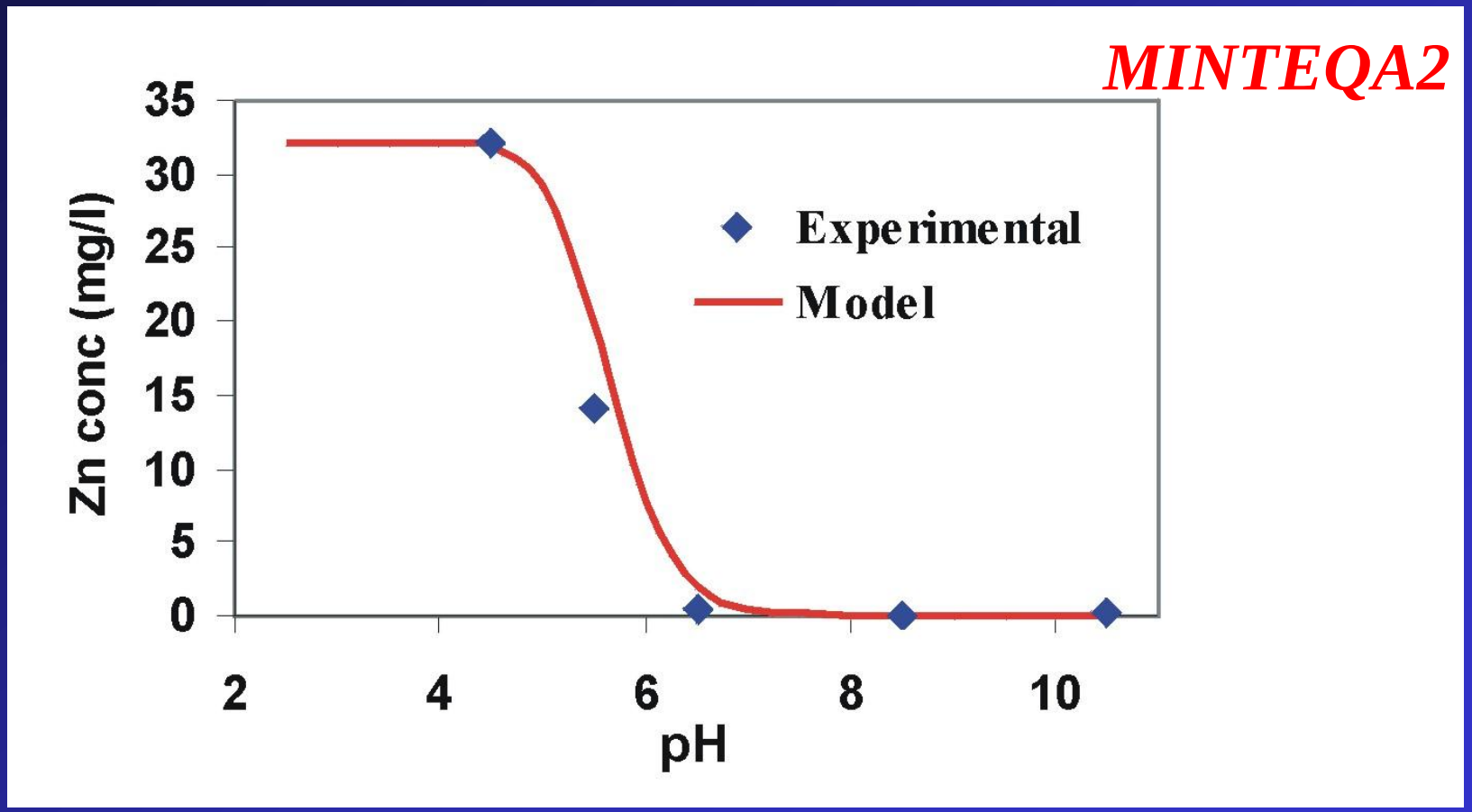

1800
1500
1200
900
600
300
0
Cu, Pb, As (mg/kg)
1
3
5
7
9
11
pH
StAm1, Cu
StAm1, Pb
StAm2, Cu
StAm2, Pb

Geochemical modelling



$Cu_3(AsO_4)_2 \cdot 6H_2O + CuO$

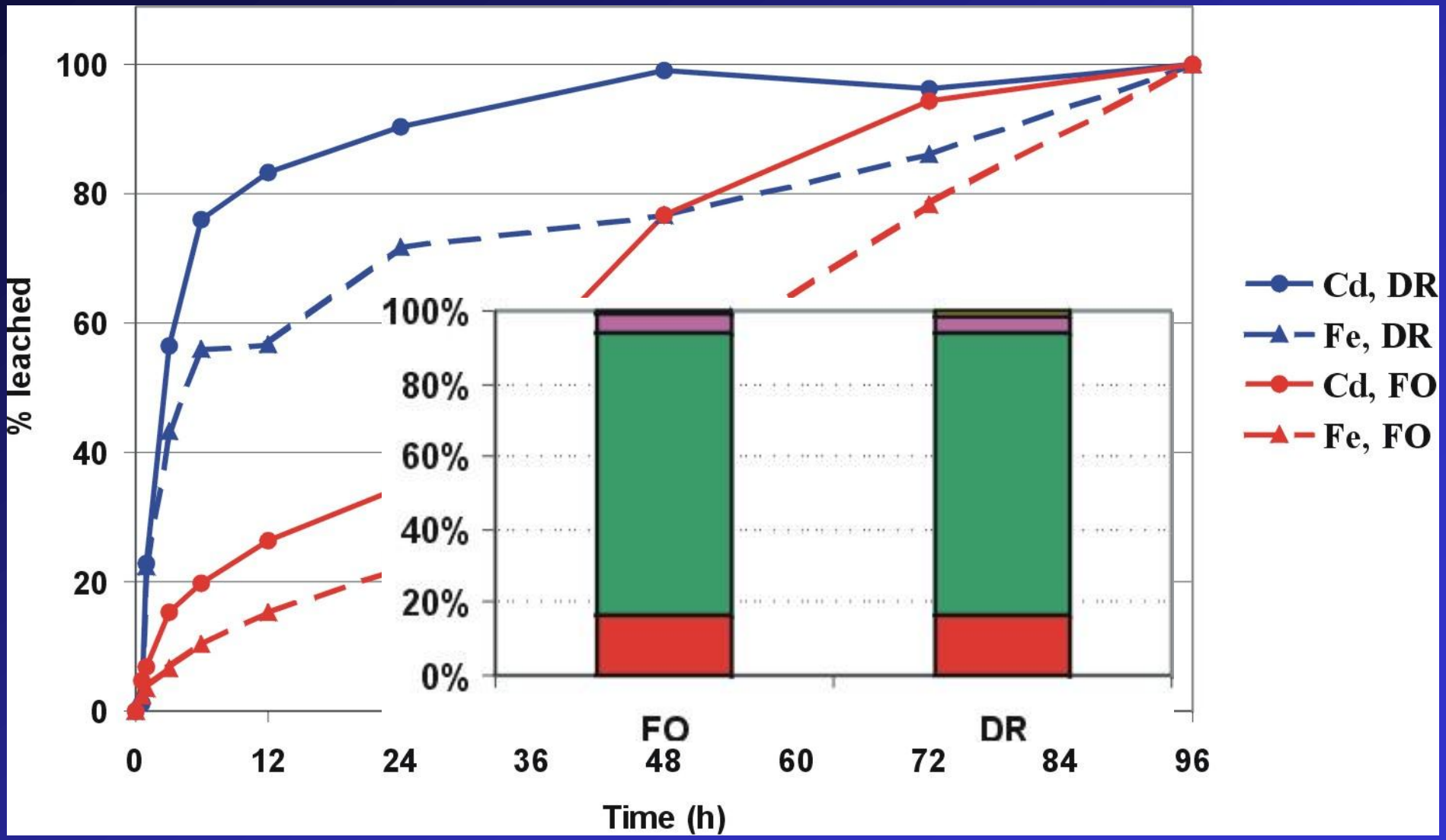
Geochemical modelling



Comparison with ‘conventional’ leaching procedures

- Single and sequential extractions
- ‘Availability test’ (NEN7340)

- Momentary mobilization
- Kinetics of heavy metal release ?
- Mechanisms of heavy metal release ?


% leached
100
80
60
40
20
0
0
12
24
36
48
60
72
84
96
Time (h)
100%
80%
60%
40%
20%
0%
FO
DR
Cd, DR
Fe, DR
Cd, FO
Fe, FO

Conclusion

- “similar samples” → different leaching behaviour
- sample mineralogy + geochemical modelling → understanding of leaching behaviour
- Kinetics of heavy metal release

Conclusion

- Assessment of long terms effects of pH
- Prediction of ‘chemical time bombs’
- Leaching behaviour → speciation
- Risk assessments
  - soil acidification
  - soil ingestion
  - accidental spills